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Studies in Overvoltage

STUDIES IN OVERVOLTAGE

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENT	1
INTRODUCTION	2
HISTORICAL	5
THEORETICAL	7
EXPERIMENTAL	8
SUMMARY	15
BIBLIOGRAPHY	16

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STUDIES IN OVERVOLTAGE.

INTRODUCTION

The measurement of overvoltage is of importance both from a theoretical and from a practical standpoint. It is important in a theoretical way in connection with the calculation of free energy values from electromotive force measurements. Such calculations of chemical affinity or decrease of free energy of a reaction are however only possible providing the process involved is a reversible one. Insofar as irreversible effects at the electrodes, ex. chemical polarization or overvoltage, appear, the calculations made from data obtained under these conditions would be correspondingly in error. It is obviously of considerable value to determine experimentally the magnitude of these irreversible effects.

In a more practical way it is to be noted that many electro chemical processes are largely dependent upon overvoltage phenomena. In the electrolytic production of gases the effect of overvoltage is such as to increase the energy consumption, i.e. the higher the overvoltage, the higher the electromotive force of decomposition which represents one of the two factors determining the electrical energy necessary to continue the process. In the production of gases, therefore, electrodes should be used which have low overvoltages.

The high overvoltage of hydrogen on lead makes the lead storage battery a reality. If lead sulphate were spread in platinum, it would be impossible to oxidize it to lead peroxide or reduce it to lead, since the desired potential could not be reached. The overvoltage of hydrogen on platinum being low means that hydrogen

would be evolved, before the potential required to affect the lead sulphate would be reached and instead of "charging the cell", the water would be decomposed.

In the mercury process for producing alkali and chlorine use is made of the fact that hydrogen has a high overvoltage on mercury. This makes possible the primary discharge of sodium ions instead of hydrogen ions. In the manufacture of electrolytic preparations different products may be obtained by varying the applied electromotive force. Since the value of this applied electromotive force depends upon the overvoltage of the electrode material, a means of varying the resulting product is available. In the reduction of nitrobenzene electrolytically, azoxybenzene, azobenzene, hydrazobenzene, and aniline may readily be prepared by regulating the applied electromotive force. In the discharge of a cell(primary or secondary) the available electromotive force is lowered by the overvoltage of the electrodes. Thus the overvoltage decreases the available electro motive force of a voltaic cell and increases the working voltage of an electrolytic cell.

From the above considerations it is evident that overvoltage plays an important role in the electrochemical industries. Often, as in the production of hydrogen it is desirable to reduce the overvoltage to a minimum, and as in the alkali manufacture a high overvoltage is necessary. Hence the study of the overvoltage produced by different metals and the factors influencing it are of great importance. Before this is possible, however, a satisfactory and consistent method for the measurement of overvoltage must be devised. Although the literature contains many data on overvoltage measurements, the methods used in obtaining the results seem more

or less at variance.

The writers, therefore, believed that further work in the development of a suitable method of measuring overvoltage would be of value. Then measurements and study of overvoltage would follow. It is unwise to carry on further work in this field without a sound and tested method.

HISTORICAL

It had been noted at an early date that the electromotive force of decomposition of water varied with the nature of the electrodes used and was always greater than the theoretical value, 1.11 volts. This phenomenon as far as can be found in the literature was first studied in detail by Caspari[1] His measurements were made by means of an arrangement that is known as the closed circuit method. That is, the electrolysing circuit is not interrupted at the time of determining the potential of the electrode under investigation. Caspari only employed this method to determine the overvoltage of different metals at the point where visible quantities of gas were evolved. Since the current necessary to obtain the above condition is very small any error due to the resistance of the solution is negligible.

The overvoltage at the time of visible gas evolution is only of theoretical importance, because in the technical industries large current densities are always employed. Attempts were therefore made to study this phenomenon at varying current densities. The apparatus used by the early investigators was of the closed circuit type. Russ[2], Sacerdote[3], Tafel[4], and others employed this method, but they substituted a tenth normal calomel electrode for a reference standard in place of a hydrogen electrode as used by Caspari. There are many other articles in the early literature which deal with this subject, but in most cases the methods used are not mentioned. It is most probable, however, that that of the closed circuit was used by them.

Newberry[5], on the other hand, employed an open circuit method in his study of overvoltage at high current densities. That is, the electrolyzing circuit is broken before measuring the potential of

the electrode under investigation. He says of the closed circuit method, "If the potential difference between the experimental electrode and the standard electrode is measured directly while the main current is flowing, the values obtained are always higher than the true overvoltage". He attributes this to the electrical resistance of the solution and also to a film of gas which is present on the surface of the electrode.

A more elaborate arrangement for the study of overvoltage is described by Watts[7]. A tapping key is used to make and break the circuit in place of the rotating commutator used by Newberry. The set-up, in addition, allows the measurement of cathodic and anodic overvoltages at the same time.

THEORETICAL

When two electrodes, one saturated with hydrogen and the other with oxygen, are made to form a voltaic cell, the potential difference between the two electrodes is found to be 1.11 volts. But when the action is reversed, i.e. when water is electrolyzed, the voltage that must be impressed in order to produce visible quantities of hydrogen and oxygen is always greater than this value, and the intensity of the applied electromotive force depends upon the metal used for the electrodes and the conditions under which the electrolysis is allowed to take place. There is a certain excess voltage which must be added before electrolysis will occur.

This increase of the back electromotive force above the normal value is the overvoltage of the cell as a whole, the increase at each electrode being termed the anodic and cathodic overvoltages respectively. This is essentially the definition given by Newberry. Caspari has designated as overvoltage the excess voltage required to cause the first hydrogen bubbles to appear as compared with a platinized platinum electrode.

When a hydrogen electrode is used as a reference standard in the measurements the cathodic overvoltage is given directly by the difference of potential existing between the hydrogen electrode and the cathode. The anodic overvoltage is found by subtracting 1.11 volts from the difference of potential existing between the hydrogen electrode and the anode.

EXPERIMENTAL

During the early period of the investigation the electrodes used were made as follows: The metal under consideration was soldered to a copper wire and the latter was placed in a piece of glass tubing The ends of the tube were then covered with sealing wax so as to prevent any of the solution from reaching the copper. Connection to the electrode was made by means of the copper wire protruding from the top of the glass tube.

The results obtained with these electrodes varied considerably. It was found that the sealing wax was affected in that it became soft and discolored. Bubbles of gas appeared on the sealing wax before forming on the metal electrode. As a striking example of the erroneous results obtained the measurements with copper electrodes are characteristic. From an apparent overvoltage of 0.26 volt which was found when bubbles first appeared the value dropped to an overvoltage of –0.05 volt when a current density of 40 milliamperes per square centimeter was applied. As a result all of the sealing wax electrodes were discarded and electrodes cut from a solid piece of the material were used.

In all of the measurements, Leeds and Northrup potentiometers and galvanometers were used. Electrolytic hydrogen was used for the hydrogen electrode. Normal sulphuric acid was used as the electrolyte in all of the measurements. The electrodes were made of the purest metal obtainable and before use were polished with No. 1 emery paper. Values for the cathodic overvoltage only were obtained.

The first method used in the measurement was that devised by Caspari. The arrangement is as shown in Fig. 1. The mean of many results obtained are given below in column 1, and for comparison

ARRANGEMENT OF APPARATUS FOR CLOSED CIRCUIT METHOD OF MEASURING OVERVOLTAGE after Caspari.

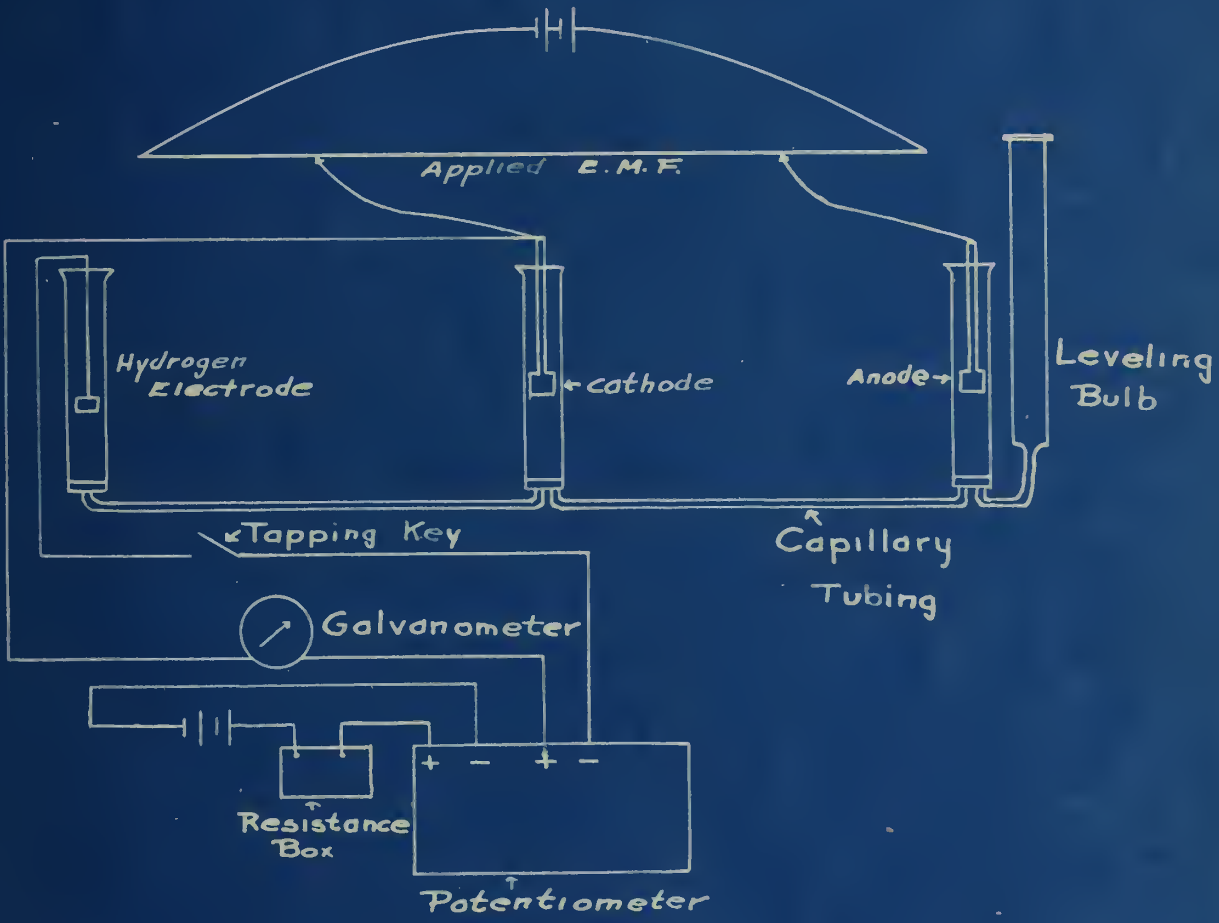

Fig 1

the values given by Caspari are listed in column 2.

	1	2
Smooth platinum	0.093	0.09
Copper	0.331	0.23
Nickel	0.194	0.21
Zinc	0.708	0.70
Lead	0.613	0.64
Mercury	0.805	0.78

The second method used was essentially that of Watts. The apparatus (Fig. 2) is so arranged that either the cathodic or the anodic potentials or the total back electromotive force of the cell could be measured. In obtaining the cathodic overvoltage switches 2 and 3 are closed to the right. S_1 was a double acting key so arranged that when up the electrolyzing circuit was made. When down, the electrolyzing circuit was broken and the potentiometer circuit made. Since this was an open circuit method, overvoltage values at different current densities could be measured. Although the time elapsing between the making and breaking of the circuits was small it was sufficient to affect the result. Consistent results were difficult to obtain, especially at high current densities. This is attributed to the fact that the time interval between the breaking and making of the circuits was a variable, depending upon the speed imparted to the key by the operator. A mean of many measurements made with this arrangement follows.

SET-UP FOR OPEN CIRCUIT METHOD USING DOUBLE ACTING KEY

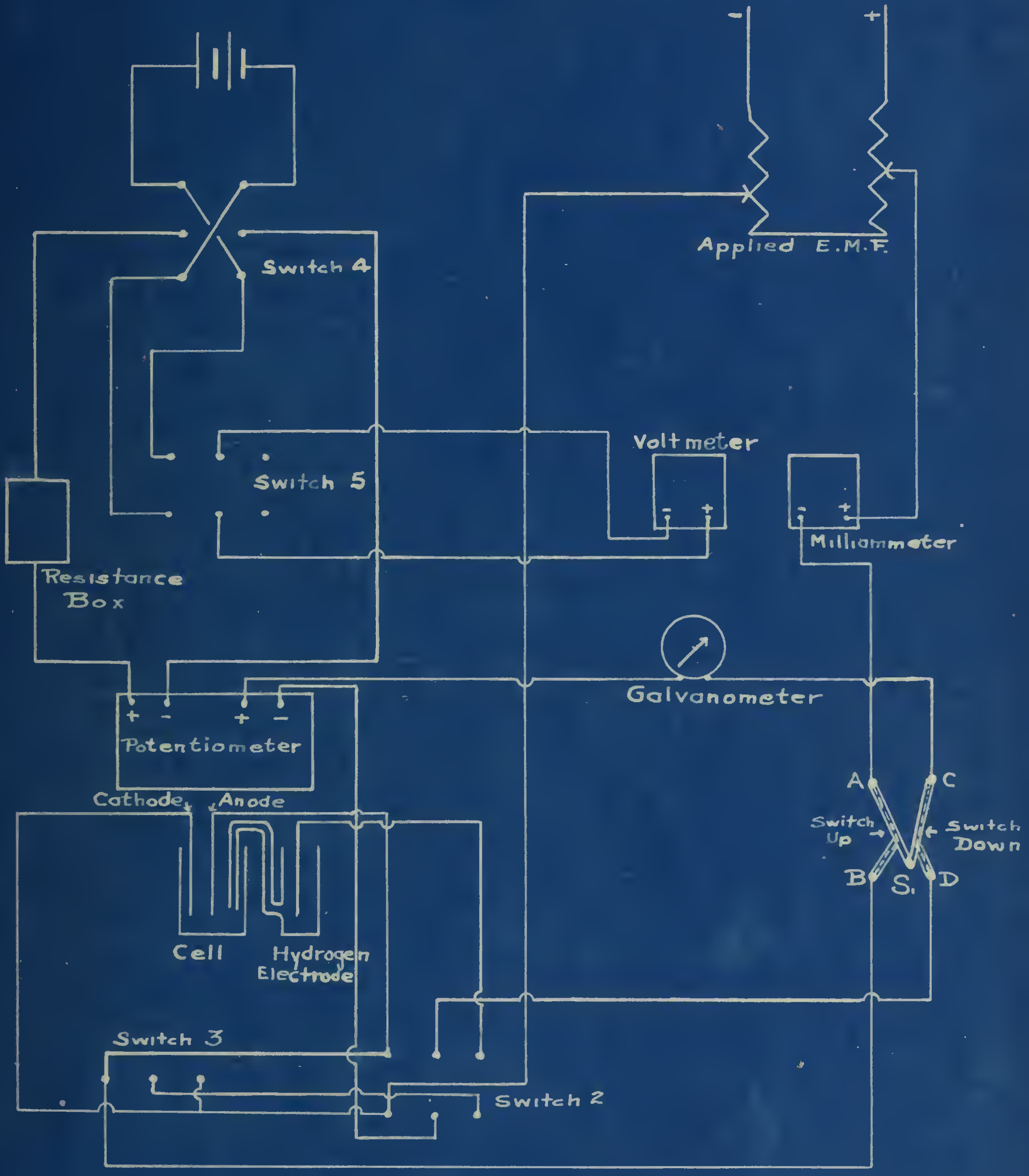

Fig. 2

Current density Milliamperes per sq. cm.	Smooth Platinum	Copper	Nickel
1	0.088	0.315	0.196
2	0.089	0.323	0.204
10	0.108	0.338	0.210
20	0.113	0.345	0.212
50	0.138	0.343	0.218
100	0.161	0.340	0.218
300	0.168	0.336	0.204
500	0.110	0.321	0.180

To avoid the inconsistency due to the different periods of time elapsing between the making and breaking of the circuits a rotary commutator was substituted for the key S_1. This commutator was so arranged that the electrolyzing circuit was made between A and B while the potentiometer circuit was broken. On revolving both circuits were left open for a short space and then the potentiometer circuit made for an equal period of time. This was essentially the device used by Newberry. However, due to the fact that the electrolyzing circuit was open more than it was closed it was difficult to read the ammeter and the results obtained were no more satisfactory than those obtained with the apparatus of Watts.

A new commutator was then devised and set up as shown in Fig. 3. The principle of the new rotary commutator was as follows. The electrolyzing circuit was made for the larger part of the revolution, broken for only a short space and again made through the potentiometer circuit for a short period. In this manner the electrolyzing circuit was made for a greater interval than

SET-UP FOR OPEN CIRCUIT METHOD USING ROTARY COMMUTATOR

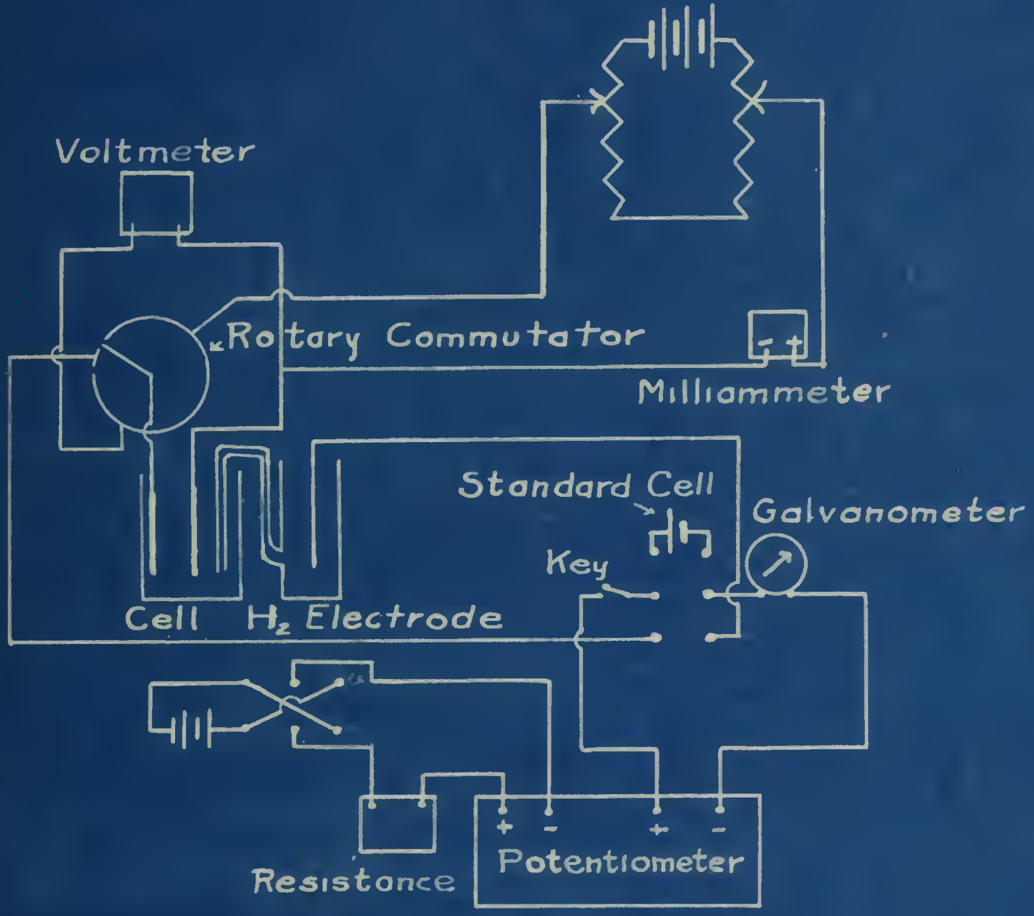

Fig. 3

it was broken, and consequently the electrodes had an opportunity to come to equilibrium. Readings of the milliamperes could be made easily and the results obtained were consistent. The following is a mean of the results obtained.

Current density Milliamperes per sq. Cm.	Smooth platinum	Nickel
1	0.054	0.184
2	0.064	
10	0.080	0.210
20	0.081	0.219
50	0.082	0.232
100	0.082	0.233
300	0.078	0.222
500	0.041	0.206

SUMMARY

1. In the measurements of overvoltage no substance other than that of the electrode under investigation should be permitted to come in contact with the electrolyzing solution.

2. Results obtained with the apparatus devised by Caspari are high in comparison with the results obtained by the open circuit method.

3. Watts' method, although applicable to high current densities does not give consistent values. The readings are only made with difficulty at high current densities.

4. With the introduction of the commutator that permitted the electrolyzing circuit to be open more then it was closed, it was also found to be unsatisfactory.

5. By the arrangement used in the latter part of the work, satisfactory results were easily obtained. The rotary commutator was so made as to allow the electrolyzing circuit to be broken for only a short interval in comparison with the time that it was made.

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